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Low emissivity high-temperature tantalum thin film coatings for silicon devices

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The authors study the use of thin (∼230 nm) tantalum (Ta) layers on silicon (Si) as a low emissivity (high reflectivity) coating for high-temperature Si devices. Such coatings are critical to reduce parasitic radiation loss, which is one of the dominant loss mechanisms at high temperatures (above 700 °C). The key factors to achieve such a coating are low emissivity in the near infrared and superior thermal stability at high operating temperatures. The authors investigated the emissivity of Ta coatings deposited on Si with respect to deposition parameters, and annealing conditions, and temperature. The authors found that after annealing at temperatures $\geq$ 900 °C the emissivity in the near infrared ($1-3\,\mu$m) was reduced by a factor of 2 as compared to bare Si. In addition, the authors measured thermal emission at temperatures from 700 to 1000 °C, which is stable up to a heater temperature equal to the annealing temperature. Furthermore, Auger electron spectroscopy profiles of the coatings before and after annealing were taken to evaluate thermal stability. A thin (about 70 nm) Ta_2O_5 layer was found to act as an efficient diffusion barrier between the Si substrate and the Ta layer to prevent Si diffusion. © *2013 American Vacuum Society*.
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I. INTRODUCTION

Silicon (Si) is a very promising platform for high-temperature MEMS based energy conversion devices, including pyroelectric, thermoelectric thermal-to-electrical energy harvesting devices, and fuel cells.[1–3] The key loss mechanisms in these systems are heat conduction and radiation; therefore, it is imperative to minimize heat losses on small device scales. Since radiative heat loss from a surface to the environment is increasing proportional to T^4 and Si has a high emissivity in the near infrared (IR) of about 0.7,[4] radiation is one of the dominant losses at high operating temperatures (above 700 °C) in Si devices.[5] However, there is a very limited body of work on high-temperature highly reflective coatings for Si devices. We have investigated a Si compatible, high-temperature, low emissivity (high reflectivity) coating to minimize radiation losses. The key challenges for such a coating are: thermomechanical stability regarding delamination, thermochemical stability regarding silicide formation and diffusion at high operating temperatures, achieving long term high-temperature stability, and high reflectivity. Metal coatings, in particular refractory metals, on Si are of interest to achieve low emissivity and reduce parasitic radiation loss in high-temperature devices. While other properties like resistivity, crystallinity, diffusion, and mechanical properties for metal coatings on Si have been investigated,[6–8] mainly for microelectronic applications, there is little literature on the optical properties of such coatings, in particular at high temperatures, and their temperature stability.

To achieve high-temperature stable low emissivity surfaces, we have chosen a multilayer platform based on a Si substrate, an optional adhesive coating, a diffusion barrier, and a low emissivity material capping material. We have investigated tantalum (Ta) as the low emissivity layer since it has a high melting point and low vapor pressure in addition to its low emissivity in the near IR (≤ 0.1 above $\sim 1\,\mu$m). We have characterized the optical properties as a function of the deposition parameters, the annealing conditions, as well as their surface roughness and sheet resistance. We have experimentally demonstrated that the emissivity can be decreased after deposition by annealing at high temperatures (above 900 °C), which is attributed to a densification process of the deposited Ta layers. In addition to room temperature (RT) emissivity, we have characterized high-temperature emission of these layers. Indeed, the emissivity is stable up to temperatures corresponding approximately to the annealing temperature. We have also investigated the role of a thin diffusion barrier layer of tantalum oxide (Ta_2O_5) on silicide formation and thermal stability, and found that it strongly inhibits Si diffusion from the substrate into the Ta layer under high-temperature treatment.

II. EXPERIMENT

Samples of Ta layers on Si were prepared by electron beam (e-beam) evaporation. The substrate was Si, and on half of the samples a 70 nm thick layer of Ta_2O_5 was deposited by e-beam evaporation at a base pressure of about 5×10^{-6} Torr, with a deposition rate of 1 Å/s. Subsequently, a layer of 230 nm Ta was deposited on both bare Si wafers

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and Si/Ta_2O_5 wafers at two different conditions: at a rate of 1 Å/s and a base pressure of 7×10^{-7} Torr (referred to as slow) and at a rate of 2 Å/s at 7×10^{-6} Torr (referred to as fast). We found that the mechanical stability of these layers was sufficient and there was no need for an adhesion coating.

Prepared samples were annealed in a tube furnace under forming gas (95% N, 5% H) atmosphere (at 0.1 Torr) to increase high-temperature stability. The base pressure before flowing the forming gas was $< 4 \times 10^{-6}$ Torr. The anneal time was 60 min at 900, 950, and 1000 °C, respectively, with a slow heating and cool down ramp of 10 °C/min.

We experimentally obtain emissivity, the key optical parameter, at room temperature both before and after annealing from reflectance measurements in the IR (1–3 μm) and from spectroscopic ellipsometry measurements in the visible and near IR (0.19–1 μm). As the prepared samples are opaque and there is no transmission in the investigated wavelength range, the emissivity E and reflectivity R amount to unity according to Kirchhoff's law: $E = 1 - R$. In addition to room temperature measurements, a Nexus 870 Fourier transform infrared spectrometer (FTIR) was used to measure emission (at normal angle) from samples heated in a vacuum chamber under forming gas atmosphere, with heater temperatures ranging from 700 to 1000 °C. To retrieve information on the oxygen content and element distribution of the deposited layers, samples before annealing and after annealing at 950 °C were examined via Auger electron spectroscopy (AES) measurements.

III. RESULTS AND DISCUSSION

A. Emissivity and annealing

The spectral emissivity for the as-deposited samples at room temperature was found to be much lower in the near IR than for Si (at high temperatures) but higher than expected for Ta[9] or tantalum silicide ($TaSi_2$)[10–12] as taken from literature (see Fig. 1). The emissivity in the measured range was found to depend first on the deposition parameters, and second on the annealing conditions, as discussed below. The difference in emissivity between the deposited Ta layers and pure Ta, as shown in Fig. 1, is attributed to the porosity and grain structure of the layers as a result of the deposition process and contamination of the layers with carbon and oxygen as found by AES. A striking difference in the near IR emissivity was found for layers deposited at different rates, the lower deposition rate of 1 Å/s leading to an emissivity that is up to 0.08 higher as compared to layers deposited at the higher deposition rate of 2 Å/s (see Fig. 1). This difference in emissivity is attributed to different material density (porosity and grain sizes) in those layers, caused by deposition. It was observed that the emissivity of samples with or without Ta oxide below the Ta layer was quite similar. The penetration depth of light δ is about 13–16 nm in the IR for Ta, defined as the distance over which the intensity of light in a material drops to 1/e of the initial value and given by $\delta = 1/\alpha = \lambda_0/(4\pi k)$, where α is the absorption coefficient and k is the imaginary part of the refractive index. The thickness of the Ta layer by far exceeds the penetration depth, and therefore Ta is the emissive layer and those samples are equivalent regarding room temperature emissivity.

After annealing samples at temperatures from 900 to 1000 °C for an hour, the emissivity measured at RT decreased in all samples. The effect was strongest after annealing at

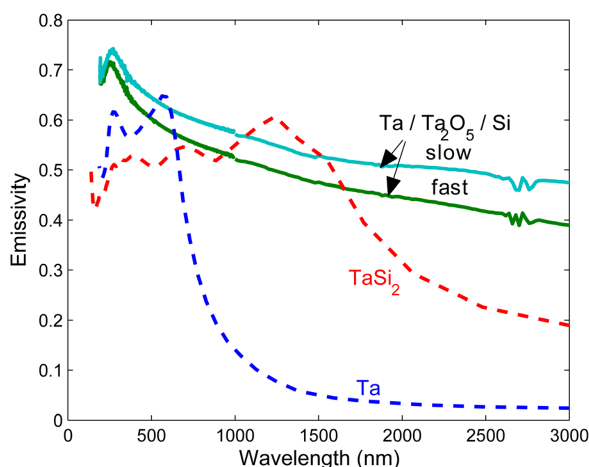

Fig. 1. (Color online) Emissivity of Ta[9] and $TaSi_2$[10] (dashed lines) as compared to measured emissivity at room temperature of as-deposited $Ta/Ta_2O_5/Si$ samples (solid lines), deposited at a rate of 2 Å/s (fast) and at a rate of 1 Å/s (slow).

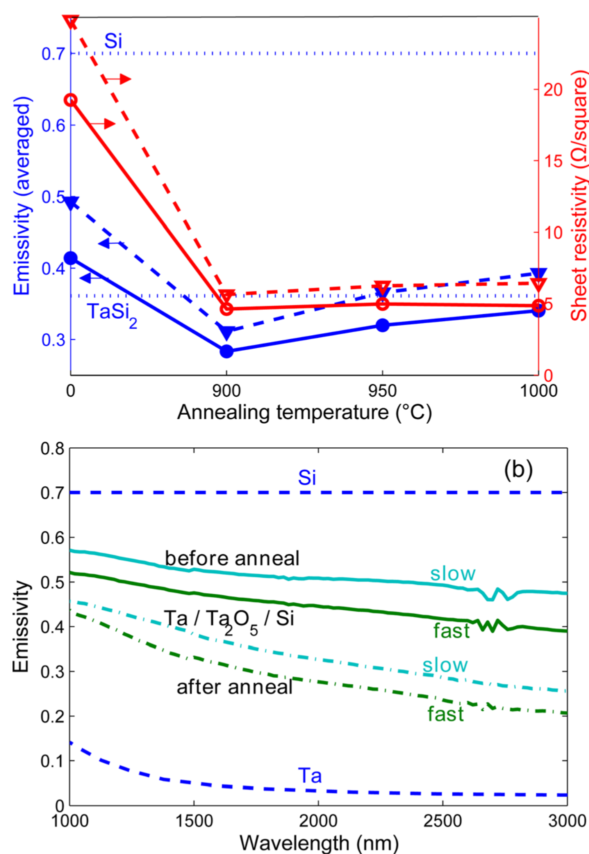

Fig. 2. (Color online) (a) Emissivity averaged over $1 - 3\ \mu$m (blue) and sheet resistance (red) before and after annealing at different temperatures for Ta/Si samples deposited at slow rate (triangles) and fast rate (circles) (lines are a guide to the eyes), and averaged emissivity of $TaSi_2$ and Si (dotted lines). (b) Emissivity spectra before annealing (solid lines) and after annealing at 900 °C (dashed-dotted lines), compared to emissivity of Ta and Si taken from literature (dashed lines).

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900 °C whereas the decrease in emissivity was weaker for higher annealing temperatures, as shown in Fig. 2. The emissivity (averaged over $1-3\,\mu$m) was 0.28 and 0.31 for fast and slow Ta/Si samples after annealing at 900 °C, respectively, 0.31 and 0.37 after annealing at 950 °C, and 0.34 and 0.39 after annealing at 1000 °C for an hour, as compared to 0.41 (fast) and 0.49 (slow) as deposited before annealing. The averaged emissivity in the near IR after annealing was smaller by about a factor of 2 than that of bare Si (with an emissivity of 0.7 above 650 °C[4]) and below that of $TaSi_2$ (average emissivity 0.37 over $1-3\,\mu$m as calculated from Ref. 12), as depicted in Fig. 2. During annealing at high temperatures, there are at least two processes taking place in parallel: first, a change in morphology, grain structure and porosity and second, an increase in surface roughness. Those two processes result in different effects on the optical properties of the sample, as discussed below.

To study the role of the morphology change, we investigated the sheet resistance of the samples before and after annealing. The decrease in the emissivity after annealing is strongly correlated to the sheet resistance of the samples, as measured by a 4-point probe. After annealing, the sheet resistance decreased to about one fourth of the original value (see Fig. 2) which indicates increased density of the layer, a decrease in porosity and a growth of grains.[13] The decrease in emissivity after annealing can be attributed to this densification with annealing at high temperatures. Following the effective medium theory,[14,15] the effective refractive index of a heterogenous medium is depending on the volume fraction of the two constituents, and limited by the Wiener bounds. As the fraction of air respective voids and grain boundaries to metal decreases with annealing in our samples, the effective refractive index increases, leading to higher reflectivity.

To investigate the correlation of emissivity and surface roughness before and after annealing, atomic force microscopy (AFM) scans of the sample surface were taken and the surface roughness R_a determined (see Fig. 3). The surface roughness increased only slightly from $R_a = 0.25$ nm before to $R_a = 0.64$ nm after annealing at 900 °C, but significantly more during annealing at 950 °C ($R_a = 2.9$ nm) and 1000 °C ($R_a = 4.7$ nm). As the roughened surface leads to more scattering and the increased air/metal fraction leads to a decrease in the refractive index, the reflectivity was decreased and hence, emissivity was increased in samples annealed at higher temperatures as compared to annealing at 900 °C. The effect of the surface roughness on the sheet resistance is negligible, as the surface roughness is small compared to the layer thickness (of about 230 nm).

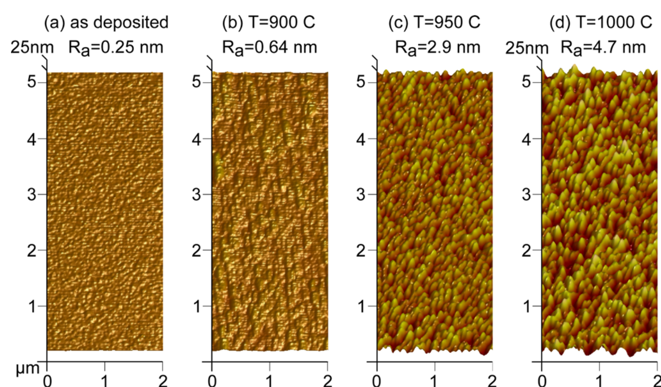

FIG. 3. (Color online) AFM images and surface roughness R_a of Ta/Si (fast rate): (a) as deposited before annealing, and after annealing for 1 h at (b) 900 °C, (c) 950 °C, and (d) 1000 °C.

In addition to the characterization of room temperature emissivity, emission measurements were performed at high temperature, at heater temperatures ranging from 700 to 1000 °C, under forming gas atmosphere with the FTIR in a range from 1 to 8 μm. Figure 4 shows the measured emission spectra at different heater temperatures. Following Planck's law of thermal radiation, the emission increases with temperature and the emission maximum shifts to shorter wavelengths at higher temperatures.

Regarding thermal stability, the measured emission showed approximately the same behavior for all samples: The sample emission was stable, i.e., constant at constant heater temperature, up to a heater temperature (which is in general higher than the temperature of the sample surface in our setup) equal to the annealing temperature (see Fig. 4). At this heater temperature, the emissivity of the samples started changing slowly over time, and emission was increasing at long wavelengths. When cooling down, the emission at lower temperature was shifted slightly to longer wavelengths as compared to the original emission at the same temperature. This implicates that the emissivity of the sample was irreversibly increased at long wavelengths ($\geq 2.5\,\mu$m) due to the high-temperature treatment, which is attributed to increased surface roughness. The temperature limit on the thermal stability of the optical properties is therefore approximately given by the annealing temperature of the tantalum layers.

Care must be taken not to change the temperature of the samples too rapidly (≤ 30 °C/min in the emission measurements), since an abrupt change in temperature may lead to precipitates, probably induced by thermal stress. XPS measurements on a sample without Ta_2O_5 layer, that showed precipitations on the surface after a fast cool down, have shown

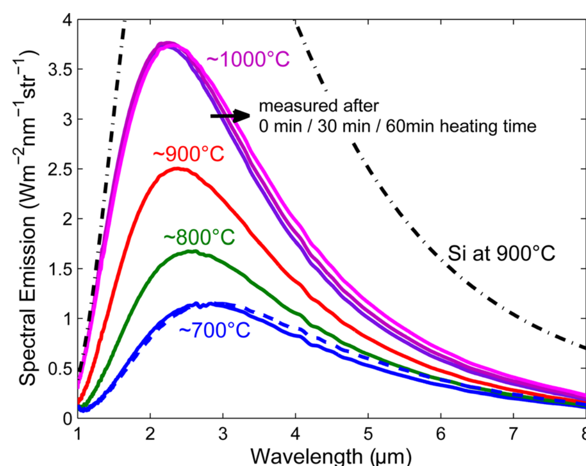

FIG. 4. (Color online) Emission spectra at different heater temperature for the Ta/Si sample (fast rate) annealed at 1000 °C. The dashed blue line is the emission of Ta/Si at a heater temperature of 700 °C after heating up to 1000 °C for 1 h. For comparison: calculated emission of Si at a sample temperature of 900 °C (black, dashed-dotted).

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these precipitates to be Si and carbon rich. AES profiles of the deposited layers confirmed the presence of C (for all samples) and Si (for samples without Ta_2O_5 layer) in the deposited layers, and their segregation toward the sample surface during high-temperature treatment.

B. AES studies and silicide formation

Previous studies have found substantial silicon diffusion and silicide ($TaSi_x$) formation at the interface of tantalum and silicon layers when exposed to elevated temperatures, starting at temperatures as low as 600 °C.[8,16–18] In Ref. 18, both the silicide formation as well as strong oxidation of Ta were observed when deposited on SiO_2 and annealed above 1000 °C. A reduction of SiO_2 and formation of tantalum oxide TaO_y and tantalum silicide $TaSi_x$ were observed even during sputter deposition of Ta on SiO_2/Si substrates at lower substrate temperatures (500 °C).[19] We anticipated a layer of Ta_2O_5 between Ta and Si to be an efficient barrier to silicide formation and thermal degradation in our approach, as Ta_2O_5 is readily formed and stable.

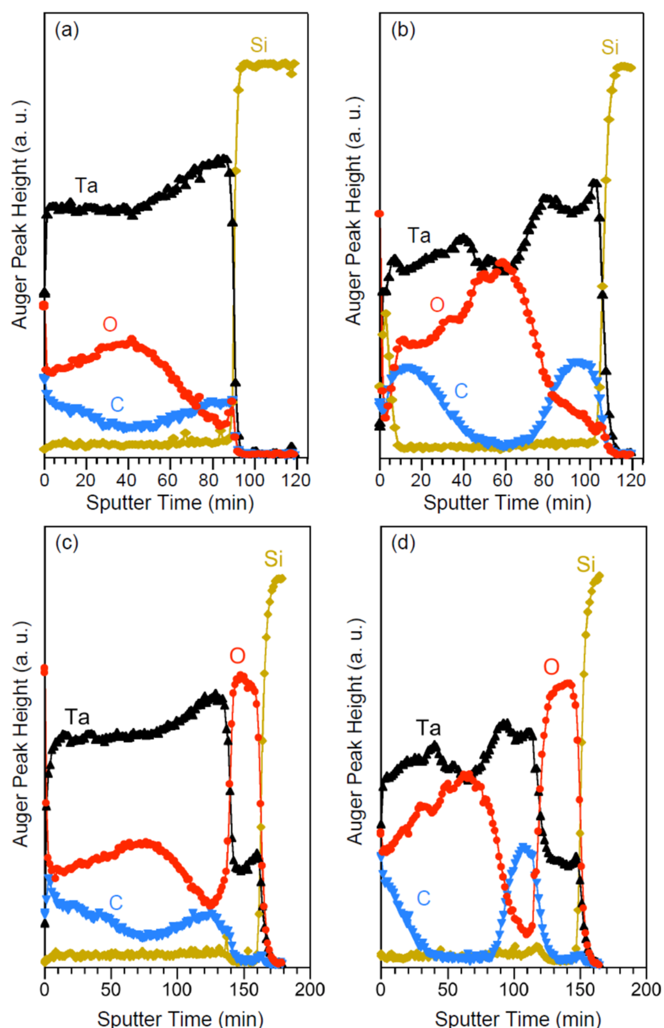

Fig. 5. (Color online) AES profiles of a Ta/Si sample without Ta_2O_5 (slow rate) (a) before and (b) after annealing at 950 °C, and of a $Ta/Ta_2O_5/Si$ sample (slow rate) (c) before and (d) after annealing at 950 °C.

AES profiles of Ta layers both on Si and on Ta_2O_5/Si (Fig. 5) showed that there is a substantial amount of oxygen and carbon incorporation in the deposited Ta layers. This contamination originated from the deposition process, and hence can be minimized by better deposition procedures of the electron beam evaporation and use of higher purity deposition material. The source of carbon was thought to be the graphite crucible, which was probably gradually contaminating the deposition material through nonideal electron beam usage, and the oxygen was associated with oxidation of the deposition material between deposition runs. The Auger profiles also showed the migration of oxygen toward the center of the Ta layer during annealing, whereas the carbon was segregating toward the interfaces both in samples with and without Ta_2O_5 layer. In the samples without Ta_2O_5, a substantial amount of Si was found on the surface after annealing [Fig. 5(b)]. Si is migrating from the substrate to the surface via grain boundary diffusion at elevated temperatures, as found in previous studies. AES showed that in these samples, it was bound as silicon oxide rather than tantalum silicide; therefore, the impact on the emissivity is low. The oxygen contamination in the deposited Ta layers could actually have been increasing the thermal stability to some extend by suppressing formation of tantalum silicide in our layers, as compared to previous studies. Still, considering long term stability, Si diffusion is undesirable as it might lead to silicide formation eventually, increasing emissivity. In those samples with Ta_2O_5 between Ta and Si, this silicon diffusion was substantially suppressed, and no Si was found on the Ta surface [Fig. 5(d)]. Therefore, a thin layer of Ta_2O_5 between the Ta and the Si substrate acts as an efficient high-temperature diffusion barrier layer.

IV. CONCLUSION

Tantalum thin film (~230 nm) layers on Si substantially decrease the emissivity (increase reflectivity) of Si in the near IR. The average emissivity in this range ($1-3\,\mu$m) after annealing (at temperatures from 900 to 1000 °C) decreased by a factor of 2 as compared to bare Si. In particular, emissivity was 0.28 and 0.31 for Ta layers deposited at 2 and 1 Å/s, respectively, after annealing at 900 °C compared to about 0.7 for Si. The emissivity of these Ta layers in the near IR depends in the first instance on the deposition parameters. We found that the emissivity in the near IR (above 1 μm) is higher than that of bulk Ta. This is due to the contamination of the Ta layers with C and O during e-beam evaporation deposition as shown by AES profiles, as well as the porosity of the deposited layers. In addition, we investigated dependence of the emissivity on the annealing temperature. The emissivity of all samples was decreased by annealing after deposition, which strongly correlated to the decrease in sheet resistance and was attributed to a change in morphology: a densification process, decreasing porosity, and grain growth at high-temperature treatment leading to both the decrease in sheet resistance and emissivity. We also found that higher annealing temperatures (>900 °C) lead to increased surface roughness, and a slight increase in

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measured emissivity as compared to lower annealing temperature (900 °C). Emission measurements at heater temperatures ranging from 700 to 1000 °C showed that the emission is stable up to a heater temperature comparable to the annealing temperature of the samples. AES profiles also showed that there is Si diffusion through the Ta layer toward the surface under high-temperature treatment, which is essentially suppressed by a thin Ta_2O_5 layer acting as a diffusion barrier between the Si substrate and the Ta layer.

These results suggest that thin Ta layers are a promising approach to a high-temperature, low emissivity coating on Si as well as potentially other substrates. An improved deposition process resulting in less contamination and higher density of the layers is anticipated to improve the presented emissivity results even further.

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